Claims

1. A method for producing a proton conducting membrane having a crosslinked structure formed by a silicon-oxygen covalent bond and having a sulfonic acid-containing crosslinked structure represented by the following formula (1) therein, which comprises a first step of preparing a mixture containing a mercapto group-containing oligomer (A) having a mercapto group and a reactive group which can form a Si-O-Si bond by condensation reaction, a second step of forming said mixture into a membrane, a third step of subjecting said membrane-like material to condensation reaction in the presence of a catalyst to obtain a crosslinked gel and a fourth step of oxidizing the mercapto group in the membrane so that it is converted to a sulfonic acid group:

$$\begin{array}{c} SO_3H \\ | \\ R^1 \\ | \\ X - Si - X \\ | \\ R^2 \end{array} \qquad (1)$$

wherein X represents -O- bond taking part in crosslinking or OH group; R^1 represents an alkylene group having 20 or less carbon atoms; R^2 represents any of CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_5, OH and -O- bond taking part in crosslinking; and R^1 and R^2 each may be mixture of different substituents.

2. The method for producing a proton conducting membrane as described in Claim 1, wherein the mercapto group-containing oligomer (A) has a plurality of mercapto groups.

3. The method for producing a proton conducting membrane as described in Claim 1, wherein the mercapto group-containing oligomer (A) is a compound represented by the following formula (5):

$$R^7O - (\underset{\substack{| \\ R^8}}{\overset{\substack{SH \\ | \\ (CH_2)_m \\ |}}{Si}} - O)_n - R^7 \qquad (5)$$

wherein R^7 represents a group selected from the group consisting of H, CH_3, C_2H_5, C_3H_7 and C_4H_9; R^8 represents a group selected from the group consisting of CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_5, OH, OCH_3, OC_2H_5, OC_3H_7 and OC_4H_9; m represents an integer of from 1 to 20; n represents an integer of from 2 to 100; R^8 may be a mixture of the same or different substituents; and R^8 may have a branched structure which is partially a -OSi bond or an intramolecular annular structure.

4. The method for producing a proton conducting membrane as described in Claim 3, wherein in the formula (5), R^8 is any of OH, OCH_3, OC_2H_5 and O-Si bond, m is 3 and n is an integer of from 3 to 50.

5. The method for producing a proton conducting membrane as described in Claim 1, wherein the mercapto group-containing oligomer (A) is a compound represented by the following formula (6):

$$R^7O - \left(\begin{array}{c} SH \\ | \\ (CH_2)_m \\ | \\ Si \\ | \\ R^8 \end{array} - O\right)_n - \left(\begin{array}{c} R^9 \\ | \\ Si \\ | \\ R^9 \end{array} - O\right)_t - R^7 \qquad (6)$$

wherein R^7 represents a group selected from the group consisting of H, CH_3, C_2H_5, C_3H_7 and C_4H_9; R^8 represents a group selected from the group consisting of CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_5, OH, OCH_3, OC_2H_5, OC_3H_7 and OC_4H_9; R^9 represents a group selected from the group consisting of OH, OCH_3, OC_2H_5, OC_3H_7, OC_4H_9, CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{11}H_{23}$, $C_{12}H_{25}$, $C_{16}H_{33}$, $C_{18}H_{37}$ and C_6H_5; m represents an integer of from 1 to 20; n represents an integer of from 1 to 100; t represents an integer of from 1 to 100; R^8 and R^9 each may be a mixture of the same or different substituents; R^8 and R^9 each may be a branched structure which is partially a -OSi bond or an annular structure; and the unit containing a mercapto group and the unit containing R^9 may exist in block or random form.

6. The method for producing a proton conducting membrane as described in Claim 5, wherein in the formula (6), n represents

an integer of from 2 to 100.

7. The method for producing a proton conducting membrane as described in Claim 5, wherein in the formula (6), R^8 represents any of OH, OCH_3, OC_2H_5 and O-Si bond, R^9 represents any of OH, OCH_3, OC_2H_5 and O-Si bond, m is 3, and the sum of n and t is an integer of from not smaller than 3 to not greater than 50.

8. The method for producing a proton conducting membrane as described in Claim 1, wherein the mercapto group-containing oligomer (A) is produced by the hydrolytic condensation of a composition containing a mercapto group-containing alkoxysilane (C) represented by the following chemical formula (2):

$$(R^3)_t(R^4)_mSi-(CH_2)_n-SH \qquad (2)$$

wherein R^3 represents a group selected from the group consisting of CH_3, C_2H_5, C_3H_7, C_4H_9 and C_6H_5; R^4 is a group selected from the group consisting of OCH_3, OC_2H_5, OC_3H_7 and OC_4H_9; t represents an integer of 0 or 1; m represents an integer of 2 or 3; the sum of m and t is 3; and n represents an integer of from 1 to 20.

9. The method for producing a proton conducting membrane as described in Claim 8, wherein in the formula (2), R^4 represents OCH_3 or OC_2H_5, t is 0, and m is 3.

10. The method for producing a proton conducting membrane as described in Claim 8, wherein in the formula (2), R^3 represents CH_3, R^4 represents OCH_3 or OC_2H_5, t is 1, and m is 2.

11. The method for producing a proton conducting membrane as described in Claim 8, wherein in the formula (2), n is 3.

12. The method for producing a proton conducting membrane as described in Claim 5, wherein the starting material composition of the mercapto group- containing oligomer (A) further contains at least one hydrolyzable silyl compound (D) represented by the following chemical formula (3):

$$Si(R^5)_4 \qquad (3)$$

wherein R^5 represents a group selected from the group consisting of Cl, OH, OCH_3, OC_2H_5, OC_3H_7, OC_4H_9 and $OCOCH_3$.

13. The method for producing a proton conducting membrane as described in Claim 12, wherein in the formula (3), R^5 is any of OCH_3 and OC_2H_5.

14. The method for producing a proton conducting membrane as described in Claim 5, wherein the starting material composition of the mercapto group- containing oligomer (A) further contains at least one hydrolyzable silyl compound (E)

represented by the following chemical formula (4):

$$(R^5)_m(R^6)_nSi \qquad (4)$$

wherein R^5 represents a group selected from the group consisting of Cl, OH, OCH_3, OC_2H_5, OC_3H_7, OC_4H_9 and $OCOCH_3$, R^6 represents a group selected from the group consisting of CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{11}H_{23}$, $C_{12}H_{25}$, $C_{16}H_{33}$, $C_{18}H_{37}$ and C_6H_5, m represents an integer of 2 or 3; and n represents an integer or 1 or 2, with the proviso that the sum of m and n is 4.

15. The method for producing a proton conducting membrane as described in Claim 1, wherein the first step further involves the blending of at least one hydrolyzable silyl compound (G) represented by the following formula (9):

$$(R^5)_m(R^6)_nSi \qquad (9)$$

wherein R^5 represents a group selected from the group consisting of Cl, OH, OCH_3, OC_2H_5, OC_3H_7, OC_4H_9 and $OCOCH_3$, R^6 represents a group selected from the group consisting of CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{11}H_{23}$, $C_{12}H_{25}$, $C_{16}H_{33}$, $C_{18}H_{37}$ and C_6H_5, m represents an integer of from 1 to 4; and n represents an integer or from 0 to 3, with the proviso that the sum of m and n is 4.

16. The method for producing a proton conducting membrane as described in Claim 15, wherein in the formula (9), R^5 represents OCH_3 or OC_2H_5, R^6 represents CH_3, m represents an integer of 3 or 4, and n represents an integer of 0 or 1, with the proviso

that the sum of m and n is 4.

17. The method for producing a proton conducting membrane as described in Claim 15, wherein in the formula (9), R^5 represents OCH_3 or OC_2H_5, m is 4, and n is 0.

18. The method for producing a proton conducting membrane as described in Claim 1, wherein the first step further involves the blending of at least one siloxane oligomer (H) represented by the following formula (10):

$$X_{3-m} - \underset{(R^{11})_m}{\underset{|}{Si}} - O - (\overset{R_{12}}{\overset{|}{\underset{R^{12}}{\underset{|}{Si}}}} - O)_n - \underset{(R^{11})_m}{\underset{|}{Si}} - X_{3-m} \qquad (10)$$

wherein X represents a group selected from the group consisting of Cl, OCH_3, OC_2H_5, OC_3H_7, OC_4H_9, OH and $OCOCH_3$; R^{11} represents a group selected from the group consisting of CH_3, C_2H_5, C_3H_7, C_4H_9 and C_6H_5; R^{12} represents a group selected from the group consisting of Cl, OH, OCH_3, OC_2H_5, OC_3H_7, OC_4H_9, $OCOCH_3$, CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{11}H_{23}$, $C_{12}H_{25}$, $C_{16}H_{33}$, $C_{18}H_{37}$ and C_6H_5; R^{12} may be a mixture of the same or different substituents; R^{12} may have a branched structure which is partially a -OSi bond or an intramolecular annular structure; m represents an integer of from 0 to 2; and n represents an integer of from 1 to 100.

19. The method for producing a proton conducting membrane

as described in Claim 1, wherein the first step further involves the blending of at least one organic-inorganic composite crosslinking agent (F) represented by the following formula (7):

$$X_{3-m} - \underset{\underset{(R^{11})_m}{|}}{Si} - R^{10} - \underset{\underset{(R^{11})_m}{|}}{Si} - X_{3-m} \qquad (7)$$

wherein X represents a group selected from the group consisting of Cl, OCH_3, OC_2H_5, OC_3H_7, OC_4H_9 and OH; R^{10} represents a C_1–C_{30} carbon atom-containing molecular chain group; R^{11} represents a group selected from the group consisting of CH_3, C_2H_5, C_3H_7, C_4H_9 and C_6H_5; and m represents an integer of 0, 1 or 2.

20. The method for producing a proton conducting membrane as described in Claim 19, wherein in the formula (7), X represents OCH_3 or OC_2H_5, R^{10} represents an alkylene chain represented by the following formula (8), and R^{11} represents CH_3:

$$-(CH_2)_n- \qquad (8)$$

wherein n represents an integer of from 1 to 30.

21. The method for producing a proton conducting membrane as described in any one of Claims 15 to 20, wherein the total added amount of at least one compound selected from the group consisting of organic-inorganic composite crosslinking agent (F), hydrolyzable metal compound (G) and siloxane oligomer (H) is 200 parts by weight or less based on 100 parts by weight

of the mercapto group-containing oligomer (A).

22. The method for producing a proton conducting membrane as described in Claim 1, wherein at the third step, the catalyst is a Bronsted acid.

23. The method for producing a proton conducting membrane as described in Claim 1, wherein at the third step, the catalyst is a basic catalyst.

24. The method for producing a proton conducting membrane as described in Claim 23, wherein the basic catalyst is an organic amine.

25. The method for producing a proton conducting membrane as described in Claim 24, wherein the organic amine is at least one compound selected from the group consisting of triethylamine, dipropylamine, isobutylamine, diethylamine, diethylethanolamine, triethanolamine, pyridine and piperazine.

26. The method for producing a proton conducting membrane as described in any one of Claims 22 to 25, wherein at the third step, as the catalyst there is additionally used at least one compound selected from the group consisting of potassium

fluoride and ammonium fluoride.

27. The method for producing a proton conducting membrane as described in Claim 1, wherein the first step further involves the blending of an oxidatively degradable, water-soluble or hydrolyzable micropore-forming agent (B) and the third step is followed by a step of removing the micropore-forming agent (B) from the membrane-like gel by oxidative degradation, dissolution or hydrolysis to form micropores in the surface and interior of the membrane.

28. The method for producing a proton conducting membrane as described in Claim 27, wherein the micropore-forming agent (B) is a liquid water-soluble organic compound.

29. The method for producing a proton conducting membrane as described in Claim 28, wherein the micropore-forming agent (B) is a polyoxyalkylene.

30. The method for producing a proton conducting membrane as described in Claim 29, wherein the micropore-forming agent (B) is a polyethylene glycol having an average molecular weight of from 100 to 600.

31. The method for producing a proton conducting membrane

as described in Claim 27, wherein the blended amount of the micropore-forming agent (B) is from 3 to 150 parts by weight based on 100 parts by weight of the mercapto group-containing oligomer (A).

32. The method for producing a proton conducting membrane as described in Claim 27, wherein the step of removing the micropore-forming agent (B) from the membrane-like gel by oxidative degradation, dissolution or hydrolysis is effected at the same time with the fourth step.

33. A method for producing a proton conducting membrane having a crosslinked structure formed by a silicon-oxygen covalent bond and having a sulfonic acid-containing crosslinked structure represented by the following formula (1) therein, which comprises a first step of oxidizing a mercapto group-containing oligomer (A) having a mercapto group and a reactive group which can form a Si-O-Si bond by condensation reaction to prepare a mixture containing a sulfonic acid group-containing oligomer (S) having at least 20 atom-% of mercapto groups in the mercapto group-containing oligomer (A) oxidized to sulfonic acid, a second step of forming said mixture into a membrane and a third step of subjecting said membrane-like material to condensation reaction in the presence of a catalyst to obtain a crosslinked gel:

$$
\begin{array}{c}
SO_3H \\
| \\
R^1 \\
| \\
X - Si - X \\
| \\
R^2
\end{array}
\qquad (1)
$$

wherein X represents -O- bond taking part in crosslinking or OH group; R^1 represents an alkylene group having 20 or less carbon atoms; R^2 represents any of CH_3, C_2H_5, C_3H_7, C_6H_5, OH and -O- bond taking part in crosslinking; and R^1 and R^2 each may be mixture of different substituents.

34. The method for producing a proton conducting membrane as described in Claim 33, wherein the total added amount of at least one compound selected from the group consisting of organic-inorganic composite crosslinking agent (F), hydrolyzable metal compound (G) and siloxane oligomer (H) is 200 parts or less by weight based on 100 parts by weight of the sulfonic acid group-containing oligomer (S).

35. A proton conducting membrane obtained by a production process as described in any one of Claims 1 to 34.

36. A fuel cell comprising a proton conducting membrane as described in Claim 35.